



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

10/019022

REC'D 21 SEP 2000

WIPO

PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99112401.7

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE,
LA HAYE, LE

15/09/00



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: 99112401.7
Demande n°:

Anmeldetag:
Date of filing: 29/06/99
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
Alusuisse Martinswerk GmbH
50126 Bergheim-Erft
GERMANY

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Process for the production of aluminium hydroxide

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:
State:
Pays:

Tag:
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
/

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:

Description

The invention relates to a new process for the production of aluminium hydroxide

5. Aluminium hydroxide in the following is widely used as fire retardant filler in glass reinforced plastics plastic composite materials, the fire safety of which is an issue of increasing importance.

10 To increase the filling level of aluminium hydroxide in order to meet the increasingly stringent fire safety requirements, it is important to be able to raise the filling level of aluminium hydroxide to ever higher levels without compromising on the physical properties of the end composite material.

15 It is well-known in the art that increased filling levels can be achieved by mixing different particle size distributions of aluminium hydroxide in order to create a more densely packed dispersion in synthetic resin (Inorganic Flame Retardants-Alone and in combinations, Rai et al. Presentation at "Flame Retardants 98", February 1998, London. In general, the wider the resulting particle size distribution (psd) the lower the viscosity and hence workability of the dispersion. However, the limitations here are that the coarser the particles of aluminium
20 hydroxide, the poorer is the surface of the finished part and the more likelihood of physical properties degradation.

25 The challenge to the industry is to achieve the high filling levels but at finer particle sizes. In addition, it is particle size and particle shape which combine to give the best possible packing so that only by exploiting the latter can the best results be obtained.

30 The problem here is that the finest particles themselves are limited in terms of complexity of particle shape adopted during crystallisation. The alternative is grind to very fine sizes but this also has limited usefulness because the crystallinity of the material is destroyed and replaced by high energy surfaces which create additional problems of high moisture content and interference with the chemistry of synthetic resins and their curing mechanisms.

Three forms of Aluminium hydroxide are known: Gibbsite (α -), Bayerite (β -) and Nordstrandite (K. Weefers and C. Misra "Oxides and Hydroxides of Aluminium" Alcoa Technical papers No. 19 Revised: 1987). Of these Gibbsite is the best known and occurs in nature as the principal constituent of bauxite. Synthetic Gibbsite is an intermediate of the Bayer process for the production of alumina from bauxite. It is prepared by seeding supersaturated sodium aluminate solution with previously crystallised Gibbsite crystals.

Bayerite does not occur in nature but it can be made in various ways, e.g., by passing carbon dioxide into sodium aluminate solution at about 20°C. However, a key property of Bayerite is that prolonged holding in such strongly alkaline conditions causes the Bayerite to transform to the more thermodynamically stable phase, (Gibbsite K. Weefers and C. Misra "Oxides and Hydroxides of Aluminium" Alcoa Technical papers No. 19 Revised: 1987).

Nordstrandite rarely occurs naturally, but it can be obtained synthetically from the gelatinous hydroxide by ageing in the presence of a chelating agent such as ethylene diamine, ethylene glycol or EDTA.

Of the three forms of aluminium hydroxide, Gibbsite is technically the most important. It is the preferred form used by the plastics industry to impart fire retardant properties to composite materials.

The crystallisation of aluminium hydroxide by the Bayer process is well known in the art. This aluminium hydroxide however is destined for calcination to alumina and smelting to aluminium metal. The coarse particles are not suitable for use as a flame retardant in plastics.

At the other end of the particle size spectrum are the fine crystals which are generally produced in a side stream process in which the crystallisation conditions are altered to create new crystals by secondary nucleation mechanism i.e., the seed crystals are very fine and specially prepared to be active in generating new nuclei.

The large gap in the middle covering a particle size of about 4 to 20 μm is normally covered via size reduction of the very large particles crystallised in the Bayer process. Thereafter, mixtures of differing psd can be created by mixing to achieve the improved packing

characteristics which lead to lower viscosities in synthetic resin, and hence higher filling levels. However, grinding to an average size of $<5 \mu\text{m}$ increasingly creates only crystalline debris with distorted surfaces.

5 A difficulty which limits the use of the very fine crystals is their pronounced tendency to aggregate and agglomerate during crystallisation. These effects are deleterious to good rheology in synthetic resins since they can increase viscosity levels dramatically. When mixed with coarser crystals to broaden the psd they cannot be incorporated at levels which can exploit their fire properties.

10 Object of the present invention therefore is to provide a process for the production of a fine crystalline aluminium hydroxide which does not incorporate the drawbacks as outlined above and known from the art.

The object could be achieved with the new process of claim 1, the Gibbsite type aluminium hydroxide obtained from the process according to claim 7 and the synthetic resin filled with
15 respective aluminium hydroxide according to claim 10.

Surprisingly, it has been found that Gibbsite crystals nucleated by Bayerite seed retain the characteristic platy pseudo-hexagonal crystal form much longer as particle size enlarges via crystal growth than do fine crystals nucleated by Gibbsite (highly active, finely ground seed). Also standard crystallisation measures taken to increase the size of the crystals further, e.g.,
20 raising the temperature and/or reducing the seed charge increase the size of the crystals with surprisingly little aggregation and/or agglomeration, which is the normal occurrence with Gibbsite crystals.

The process of the present invention is characterised in that a liquor obtained from the Bayer
25 process is seeded with Bayerite crystals subsequently stirred under precipitation of the Gibbsite type aluminium hydroxide and thereafter the solid obtained in suspension is filtered off.

The liquor from the Bayer process can be defined by a molar ratio Na_2O to Al_2O_3 from 1,4 to
30 1,55, preferably from 1,45 to 1,50.

The Bayerite crystals used for the seed expediently have a grain diameter in the 50% range d_{50} of $1,2 \mu\text{m}$ to $2,2 \mu\text{m}$, preferably of $1,5 \mu\text{m}$ to $1,8 \mu\text{m}$. They can further be characterised by

a grain diameter in the 10% range d_{10} of 0,5 μm to 0,9 μm , preferably of 0,6 μm to 0,8 μm a grain diameter in the 90% range d_{90} of 3,5 μm to 5,5 μm , preferably of 4,0 μm to 4,5 μm .

5 The Bayerite crystals used for the process according to the invention can be obtained by seeding a pregnant Bayer liquor having a molar ratio Na_2O to Al_2O_3 as given above and having been cooled to a temperature of 20°C to 25°C with 2 g/l to 3 g/l of Bayerite crystals previously obtained.

10 The suspension as a rule will be stirred for a period of 15 to 25 hours but at least until the solid content has risen to 60 g/l to 120 g/l.

The crystals in this suspension show an average particle size of 5 to 15 μm and a specific surface area according to BET of 5 to 10 m^2/g .

After filtering, washing the crystals with water and resuspending them in water, the suspension passes a size reduction treatment to lower the average crystal size to <1 μm and to
15 raise the specific surface area according to BET to > 20 m^2/g .

Size reduction treatment can happen in mills customarily employed for this kind of milling like in bead mills

The crystals obtained are characterised as described above.

20 Seeding as a rule is effected by adding the Bayerite crystals obtained, to the Bayer liquor at a temperature of the Bayer liquor of 50°C to 70°C and in an amount relating to the Bayer liquor of 1 g/l to 3 g/l.

During crystallisation the Bayerite seed is fully transformed to Gibbsite.

25 Precipitation usually takes place under stirring and will be continued until after the molar ratio Na_2O to Al_2O_3 is in the range of 2,2 to 3,5, preferably from 2,5 to 3,0.

The precipitated Gibbsite type aluminium hydroxide can easily be collected by filtration

30 The Gibbsite type crystalline aluminium hydroxide prepared with the process of the present invention shows the following characteristics:

Grain diameter in the 50% range d_{50} of 1,5 μm to 4,5 μm , preferably of 1,8 μm to 4,0 μm , in the 10% range d_{10} of 0,4 μm to 2,0 μm , preferably of 0,5 μm to 1,8 μm and in the 90% range d_{90} of 3,0 μm to 9,5 μm , preferably of 3,5 μm to 9,0 μm .

Specific surface area according to BET is in the range of 1,0 m^2/g to 4,0 m^2/g , preferably of

5. 2 m^2/g to 3 m^2/g .

Aspect ratio which is the ratio length to thickness of a crystal is about 4 to 6:1.

10 The crystalline Gibbsite type aluminium hydroxide obtained with the process of the present invention can either alone or as part of a mixture be filled into synthetic resins, preferably into thermosetting plastics, such as unsaturated polyester resins or epoxy resins. Extraordinarily high filling levels of 150 phr to 200 phr can be achieved.

15 In order to achieve high filling levels but at finer particle sizes usually mixtures of different psd's of aluminium hydroxides are applied. The Gibbsite type aluminium hydroxide crystals obtained from the process of the invention are ideally suited to be mixed with ground materials from coarse aluminium hydroxide obtained from the Bayer process. On size reduction coarse aluminium hydroxides increasingly adopt a plate like form due to gross fracture, due to grinding, parallel to the basal planes of the blocky hexagonal prisms. Preferably the mixtures have a grain diameter in the 50% range d_{50} of 4 to 20 μm .

20

The following examples illustrate the invention.

Examples

Example 1

- A sodium aluminate solution having a temperature of 60 °C and composed of 140 g/l Na₂O, 150 g/l Al₂O₃ and 160 g/l of total soda was seeded with 2g/l of Bayerite crystals having the following characteristics:
- Grain diameter in the 50% range $d_{50} = 1,6 \mu\text{m}$
Grain diameter in the 10% range $d_{10} = 0,75 \mu\text{m}$
Grain diameter in the 90% range $d_{90} = 4,25 \mu\text{m}$
- The Bayerite crystals have previously been obtained by cooling a sodium aluminate solution having a temperature of 20 to 22°C and composed of 140 g/l Na₂O, 155 g/l Al₂O₃ and 160 g/l of total soda (molar ratio Na₂O to Al₂O₃ 1,48) with 2 to 3g/l of Bayerite crystals. Stirring of the suspension for a period of 20 h took place until the solids content has risen to 100 g/l. The suspended Bayerite crystals have a grain diameter in the 50% range d_{50} of 1,6 μm and a BET surface of 3,4 m²/g. After filtering the suspension, washing the crystals with water and resuspending the crystals in water (concentration ca. 100 g/l) size reduction in a bead mill was accomplished

Mill parameter:

- | | |
|---------------|-----------------|
| Mill type: | Backofen |
| Capacity: | 200 l |
| Beads: | 1,5 mm diameter |
| Total Charge: | 80% |
| Throughput: | 2000 – 3000 l/h |

The crystals so obtained were filtered off and had the characterisation as herein above described.

After a retention time of 48 hours at 60°C 100 g/l Gibbsite type aluminium hydroxide was obtained, the Bayerite seed was fully transformed to Gibbsite during the crystallisation period. The following table shows the influence of changing Bayerite seed charge and crystallisation temperature on the grain diameter in the 50% range d_{50} of the Gibbsite type aluminium hydroxide obtained and the largest particle size present (top cut).

The comparison examples were performed following the same procedure as described herein above with the exception that the seed material was Gibbsite.

Table 1

5

Example	Seed charge (g/l)	Cryst. Temp. (°C)	d ₅₀ product (µm)	Top cut (µm)
1 (invention)	1	60	2.8	7
2 (invention)	2	60	1.8	6
3 (invention)	3	60	1.6	6
4 (invention)	1	65	3.6	8
5 (invention)	1	70	4.1	9
6 (invention)	2	70	3.5	8
7 (comparison)	8	60	1.4	7
8 (comparison)	6	60	2.1	9

Example 9:

- 10 The effect of the different product forms was tested on rheology in synthetic resin. 150 parts per hundred (phr) of the product of examples 2 (invention), 6 (invention), 7 (comparison) and 8 (comparison) were introduced in the unsaturated polyester resin Synolite 002-N-2 of DSM BASF. Viscosity was measured with a Brookfield HBT viscosimeter at 23°C.

15 **Table 2**

Product of example	Viscosity (mPas)	Viscosity measurement conditions
3 (Invention)	60	spindle 3 at 5 rpm
6 (Invention)	70	spindle 4 at 10 rpm
7 (Comparison)	750	spindle 7 at 10 rpm
8 (Comparison)	1500	spindle 7 at 10 rpm

Example 10

Following example 9, rheology in synthetic resin was tested with mixtures of Gibbsite type aluminium hydroxides according to the invention and coarse size reduced aluminium

- 5 hydroxide crystals obtained from the Bayer process. Comparison was made against a mixture of a fine Gibbsite seeded aluminium hydroxide and coarse size reduced aluminium hydroxide crystals obtained from the Bayer process.

- 10 175 parts per hundred (phr) of a 1:1 mixture (d_{50} 4 μm) of the product of example 2 (invention) and of MARTINAL®ON-310 (Alusuisse Martinswerk GmbH, D-Bergheim) having a d_{50} of 10 μm was introduced in the unsaturated polyester resin Synolite 002-N-2 of DSM BASF. Viscosity was measured with a Brookfield HBT viscosimeter at 23°C.

- 15 175 parts per hundred (phr) of a 1:1 mixture (d_{50} 4 μm) of the product of example 7 (comparison) and of MARTINAL®ON-310 (Alusuisse Martinswerk GmbH, D-Bergheim) having a d_{50} of 10 μm was introduced in the unsaturated polyester resin Synolite 002-N-2 of DSM BASF. Viscosity was measured with a Brookfield HBT viscosimeter at 23°C.

- 20 The results are shown in table 3.

Table 3

Mixture containing	Viscosity (mPas)	Viscosity measurement conditions
Example 2 (invention)	65	spindle 5 at 20 rpm
Example 7 (comparison)	220	spindle 6 at 10 rpm

Example 11

- 175 parts per hundred (phr) of a 1:2 mixture (d_{50} 14 μm) of the product of example 6 (invention) and of MARTINAL[®]ON-320 (Alusuisse Martinswerk GmbH, D-Bergheim) having a d_{50} of 20 μm was introduced in the unsaturated polyester resin Synolite 002-N-2 of DSM BASF. Viscosity was measured with a Brookfield HBT viscosimeter at 23°C.

- 175 parts per hundred (phr) of a 2:1 mixture (d_{50} 14 μm) of the product of example 7 (comparison) and of MARTINAL[®]ON-320 (Alusuisse Martinswerk GmbH, D-Bergheim) having a d_{50} of 20 μm was introduced in the unsaturated polyester resin Synolite 002-N-2 of DSM BASF. Viscosity was measured with a Brookfield HBT viscosimeter at 23°C.

The results are shown in table 4.

15 **Table 4**

Mixture containing	Viscosity (mPas)	Viscosity measurement conditions
Example 6 (invention)	28	spindle 5 at 50 rpm
Example 7 (comparison)	42	spindle 3 at 5 rpm

Example 12

- 20 175 parts per hundred (phr) of a 1:1:1 mixture (d_{50} 18 μm) of the product of Example 1 (invention), of ground grade (d_{50} 20 μm , MARTINAL[®] ON-320) and with unground grade (d_{50} 55 μm , MARTINAL[®] ON, Alusuisse Martinswerk GmbH, D-Bergheim) was introduced into the Synolite 002-N-2 unsaturated polyester resin of DSM BASF.

- The viscosity of this mix was compared with that of another mix in which the product of Example 8 (comparison) was substituted for the product of Example 1 (invention). The viscosities were measured by Brookfield viscosimeter at a temperature of 23°C. The results are given in Table 5.

Table 5

Mixture containing	Viscosity (mPas)	Viscosity measurement conditions
Example 1 (invention)	20	spindle 5 at 50 rpm
Example 8 (comparison)	29	spindle 5 at 50 rpm

Example 13

5

125 parts per hundred (phr) of a 1:3 mixture (d_{50} 16 μm) of the product of Example 4 (3,6 μm) and the milled grade (20 μm ; MARTINAL[®] ON-320, Alusuisse Martinswerk GmbH, D-Bergheim) was introduced into the epoxy resin Araldite GY 260 of Ciba Polymers. The viscosity of this mix was compared with another in which the product of Example 4 was substituted by the product of Example 8 (comparison). Viscosities were measured at a temperature of 23°C by means of a Brookfield viscosimeter. The results are shown in Table 6.

10

Table 6

Mixture containing	Viscosity (mPas)	Viscosity measurement conditions
Example 4 (invention)	82	spindle 5 at 10 rpm
Example 8 (comparison)	140	spindle 5 at 10 rpm

Claims:

1. Process for the preparation of Gibbsite type aluminium hydroxides characterised in that a liquor obtained from the Bayer process is seeded with Bayerite crystals.
2. Process according to claim 1, characterised in that the Bayer liquor has a molar ratio Na_2O to Al_2O_3 from 1,4 to 1,55.
3. Process according to claims 1 to 2, characterised in that the Bayerite crystals have a grain diameter in the 50% range d_{50} of 1,2 μm to 2,2 μm .
4. Process according to any one of claims 1 to 3, characterised in that the Bayerite crystals have a grain diameter in the 10% range d_{10} of 0,5 μm to 0,9 μm and in the 90% range d_{90} of 3,5 μm to 5,5 μm .
5. Process according to any one of claims 1 to 4, characterised in that the Bayerite crystals are added at a temperature of the liquor of 50°C to 70°C in an amount of 1 g/l to 3 g/l.
6. Process according to any one of claims 1 to 5, characterised in that after seeding the process mixture is stirred under precipitation until the molar ratio of Na_2O to Al_2O_3 is reaching the range of 2,2 to 3,5.
7. Gibbsite type aluminium hydroxide having the following characteristics defined by a grain diameter in the 50% range d_{50} of 1,5 μm to 4,5 μm , in the 10% range d_{10} of 0,4 μm to 2,0 μm , in the 90% range d_{90} of 3,0 μm to 9,5 μm .
8. Gibbsite type aluminium hydroxide according to claim 7 further defined by a surface area according to BET of 1,0 m^2/g to 4,0 m^2/g and an aspect ratio of 4 to 6:1.
9. Mixture of Gibbsite type aluminium hydroxides, characterised in that it has a grain diameter in the 50% range of d_{50} 4 to 20 μm and contains a Gibbsite type aluminium hydroxide according to claim 7 or 8 or a Gibbsite type aluminium hydroxide obtained according to the process of claims 1 to 7.

10. Synthetic resin containing a Gibbsite type aluminium hydroxide according to claims 7 or 8 or obtained according to the process of claims 1 to 7.

5 11. Use of a Gibbsite type aluminium hydroxide according to claim 7 or 8 or obtained according to the process of claims 1 to 7 as fire retardant additive in synthetic resins.

Abstract:

Gibbsite type aluminium hydroxides are obtained from seeding a Bayer liquor with Bayerite crystals.

- 5 · Then Gibbsite type aluminium hydroxides show excellent properties as fire retardant fillers in synthetic resins.

10

15

20

25

30

Basel, June 29, 1999

SREP / B. Rauber / slu / LA

